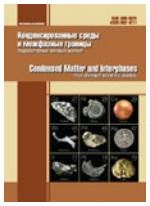

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Phase transformations during the annealing of Ga_2O_3 films

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Abstract

A growth technique has been developed to obtain the three main crystalline phases of Ga_2O_3, namely: α-phases, ε-phases, and β-phases using hybrid vapour phase epitaxy (HVPE). The substrate temperatures and precursor fluxes were determined at which only the α-phase, only the ε-phase, or only the β-phase were deposited. It was found that the annealing of the metastable α- and ε-phases led to completely different results. The ε-phase quickly transforms into the stable β-phase as a result of annealing, while the α-phase, upon annealing, transforms into an intermediate amorphous phase, after which it peels off and is destroyed. The obtained result is explained by the fact that the reconstructive phase transition from the α-phase into the β-phase is accompanied by too large an increase in density (~10%), leading to enormous elastic stresses and, consequently, an increase in the height of the phase transition barrier.

Keywords: Reconstructive phase transitions, Gallium oxide, Polymorphs, X-ray diffraction, Spectroscopic ellipsometry, Raman spectrum

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1. Introduction

In recent years, there has been enormous interest in the growth of so-called transparent conductors, which are often metal oxides such as zinc oxide ZnO, magnesium oxide MgO, gallium oxide Ga_2O_3 and some other oxides [1]. Among these materials, gallium oxide Ga_2O_3 [2–4], which is a semiconductor with a large band gap ~ 5 eV, characterized by very high breakdown voltage ~ 8 $Mvcm^{-1}$ is distinguished. It is easily doped, which makes it very promising for micro- and optoelectronics applications. In addition, it is easy to mix with the magnetic material Cr_2O_3, which makes it promising for spintronics. Another important feature of Ga_2O_3 is its existence in several crystalline modifications. Reviews [2–4] indicate 5 phases as the main ones, namely, the stable β-phase with monoclinic structure C2/m and metastable the ε-phase with orthorhombic structure $Pna2_1$, the α-phase with a rhombohedral structure $R\bar{3}c$ (corundum structure), the δ-phase with a body-centred cubic structure $la\bar{3}$, and the γ-phase with a cubic structure $Fd\bar{3}m$. Despite the fairly large number of metastable phases, it is extremely difficult to obtain them, since mainly only the stable β-phase grows. Currently, a fairly large number of Ga_2O_3 growth methods have been developed. These are various technologies for the volumetric growth of Ga_2O_3, and methods of molecular beam epitaxy, and chemical vapour deposition, as well as methods of chloride-hydride vapour epitaxy [5–7]. Usually, Al_2O_3 sapphire crystals with different orientations, silicon carbide [8], as well as silicon are used as substrates for the growth of Ga_2O_3 layers. Silicon, which is used quite often, is not a very good choice for Ga_2O_3 growth, since it can conduct electric current and Ga_2O_3 grows much worse on it. Firstly, silicon poorly orients growing Ga_2O_3 layers, secondly, oxygen O_2 and water H_2O when used as reagents for the production of Ga_2O_3, react with silicon to form amorphous silicon dioxide SiO_2, which further worsens the epitaxy of Ga_2O_3. Therefore, in this study, Al_2O_3sapphire (0001) was used as the substrate.

The purpose of this study was the investigation of solid-phase transformations between various polymorphs of Ga_2O_3. In the study [7] a method for obtaining the three main phases of Ga_2O_3 was developed, namely, the stable β-phase, the metastable α-phase and the metastable ε-phase by chloride-hydride epitaxy on SiC-3C/Si hybrid substrates at different temperatures. In this study, these three phases were obtained by a similar method, but in this case using sapphire Al_2O_3, which is especially important for α-phases, since it has the same corundum structure as sapphire. As a result, the quality of the resulting phases was significantly higher, which made it possible to study the various optical properties of Ga_2O_3 phases by ellipsometry and Raman spectroscopy methods. Next, the metastable α-phase and the ε-phase were annealed at different temperatures in order to transform them into a stable β-phase. All phases were studied in detail by X-ray diffraction, Raman spectroscopy, and spectral ellipsometry.

2. Experimental

Standard sapphire substrates with the orientation <0001> were used for the growth of Ga_2O_3 layers. Ga_2O_3 layers were grown using hydride vapour phase epitaxy (HVPE) due to the following chemical reaction [7]:

$$2GaCl + 3/2O_2 = Ga_2O_3 + Cl_2. \quad (1)$$

Gallium chloride was synthesized directly in the source zone of the reactor by passing hydrogen chloride gas (HCl 99.999%) over gallium metal (Ga 99.9999%). The yield of the GaCl synthesis reaction was approximately 85%. The oxygen necessary for the formation of gallium oxide was supplied in a mixture with argon (20% oxygen, 80% argon). The synthesis of gallium oxide was carried out under conditions of excessive oxygen flow. The ratio of components of groups VI/III was in the range of 3–5. The rate of Ga_2O_3 deposition was determined by the HCl flow through the gallium source and depended on the deposition temperature, which varied over a wide range of 500–1000 °C. With total gas flow ~ 5 000 cm^3/min Ga_2O_3 deposition rate started from approximately 0.4–0.5 μm/min at 500 °C and ended at 0.8–1.0 μm/min at 1000 °C [7]. The deposition time was chosen to be approximately 2–4 min in order to obtain a Ga_2O_3 layer approximately ~2 μm thick. After growth was completed, the substrate was cooled in an argon flow to room temperature. The results of the analysis showed that different phases of Ga_2O_3 were synthesised

at different temperatures. At 800–1000 °C, Ga_2O_3 precipitated in the stable β-phase, as in the vast majority of other experiments [3,4,9]. At a synthesis temperature of 550–600 °C, Ga_2O_3 precipitated only in the metastable ε-phase. At synthesis temperature of 500–520 °C, Ga_2O_3 deposited only in the metastable α-phase. X-ray diffraction patterns of three Ga_2O_3 samples, grown on Al_2O_3 (0001) at temperatures of 510, 575, and 900 °C respectively are shown in Fig. 1. It is clearly seen that in the first case Ga_2O_3 was deposited in the most symmetrical α-phase with a rhombohedral structure $R\bar{3}c$, in the second case Ga_2O_3 deposited in the least symmetrical ε-phase with the orthorhombic structure $Pna2_1$, and in the third case Ga_2O_3 deposits in a stable β-phase with a monoclinic structure C2/m.

3. Results and discussion

The dependence of permittivity on photon energy plays an important role in the optical properties of materials [7], therefore it was measured for all three Ga_2O_3samples using a M-2000D J.A. Woollam ellipsometer with a rotating compensator operating in the range of 0.75–6.45 eV. The measured dependence is presented in Fig. 2. Based on the imaginary part of the dielectric permittivity ε_2 associated with light absorption, we can conclude that the β-phase absorbs light most strongly and has the lowest band gap. The most symmetrical α-phase, on the contrary, was the most transparent and had the largest band gap. The least symmetric ε-phase occupied an intermediate position in terms of transparency and band width (in all three cases, the band gap was indirect). The result obtained is in full agreement with the results of calculations by the quasi-particle method (GW) [10].

The Raman spectrum of all three phases measured using a WiTec Alpha300R confocal Raman microscope is shown in Fig. 3. The main basic lines are signed. In addition to the lines corresponding to the Ga_2O_3 phases, there are sapphire lines, since at the laser wavelength of 532 nm all phases of Ga_2O_3 are transparent. The measured spectra are in very good agreement with the theoretical spectra computed by the density functional theory (DFT) [7].

Next, samples of the metastable α- and ε-phases were kept in a vacuum at various

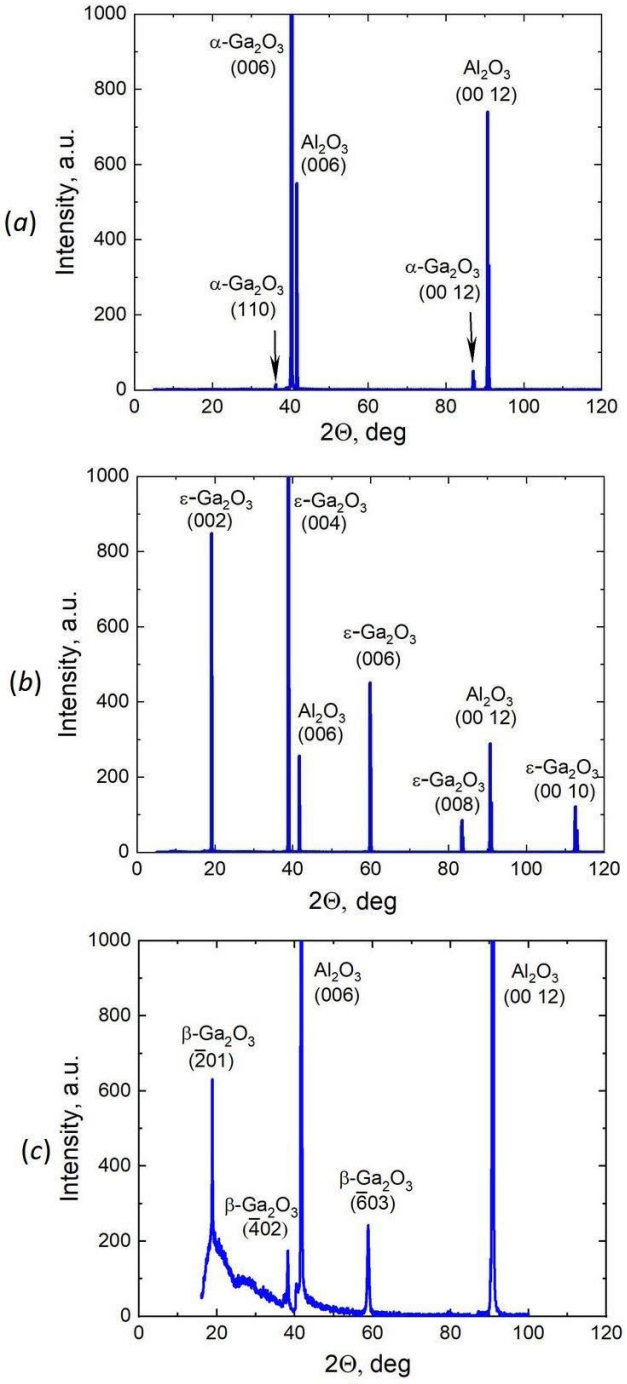

Fig. 1. X-ray diffractograms of three Ga_2O_3 samples grown on Al_2O_3(0001) sapphire at temperatures of 510 (a), 575 (b), 900 °C (c)

temperatures from 650 to 950 °C. The annealing time varied from 10 to 30 min. The resulting samples were again studied by X-ray diffraction, Raman spectroscopy, and spectroscopic ellipsometry. The research results were as follows. The metastable ε-phase transforms into a stable

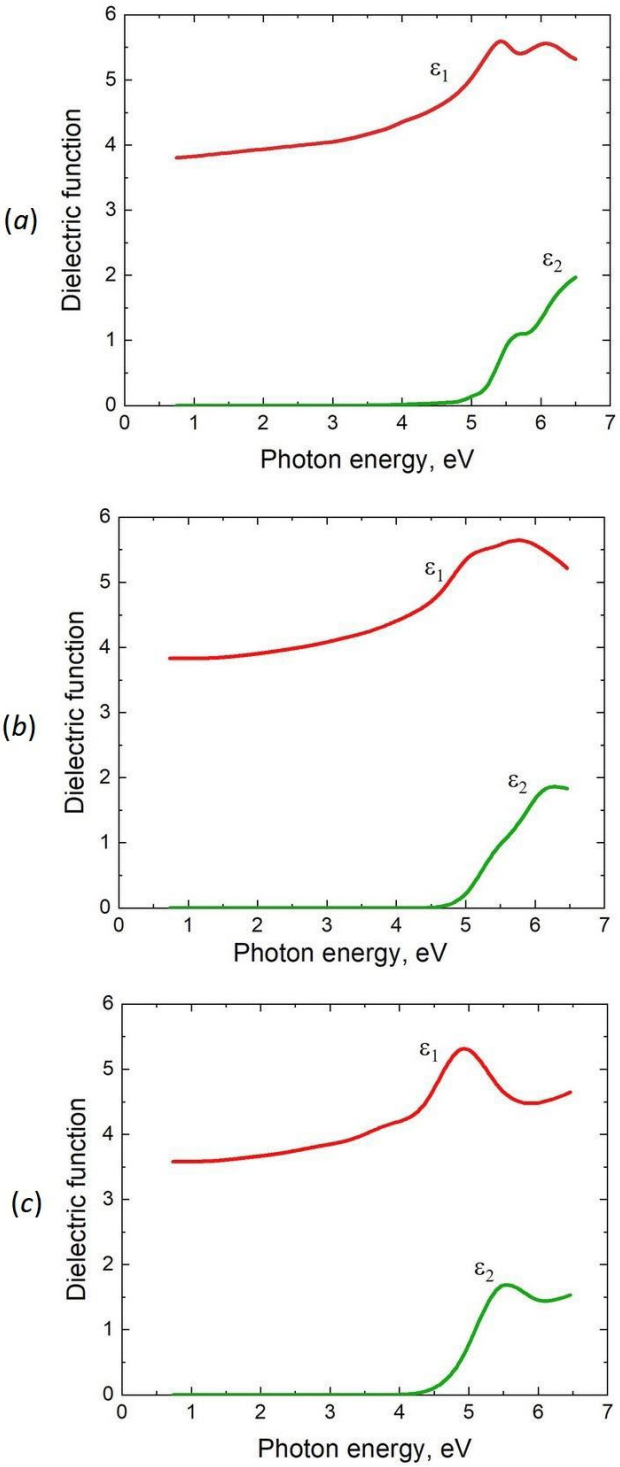

Fig. 2. Dependence of the dielectric constant of three Ga_2O_3 samples grown on Al_2O_3(0001) sapphire at temperatures of 510 (a), 575 (b), 900 °C (c) on the photon energy. ε_1 is the real part of the dielectric constant, ε_2 is the imaginary part of the dielectric constant

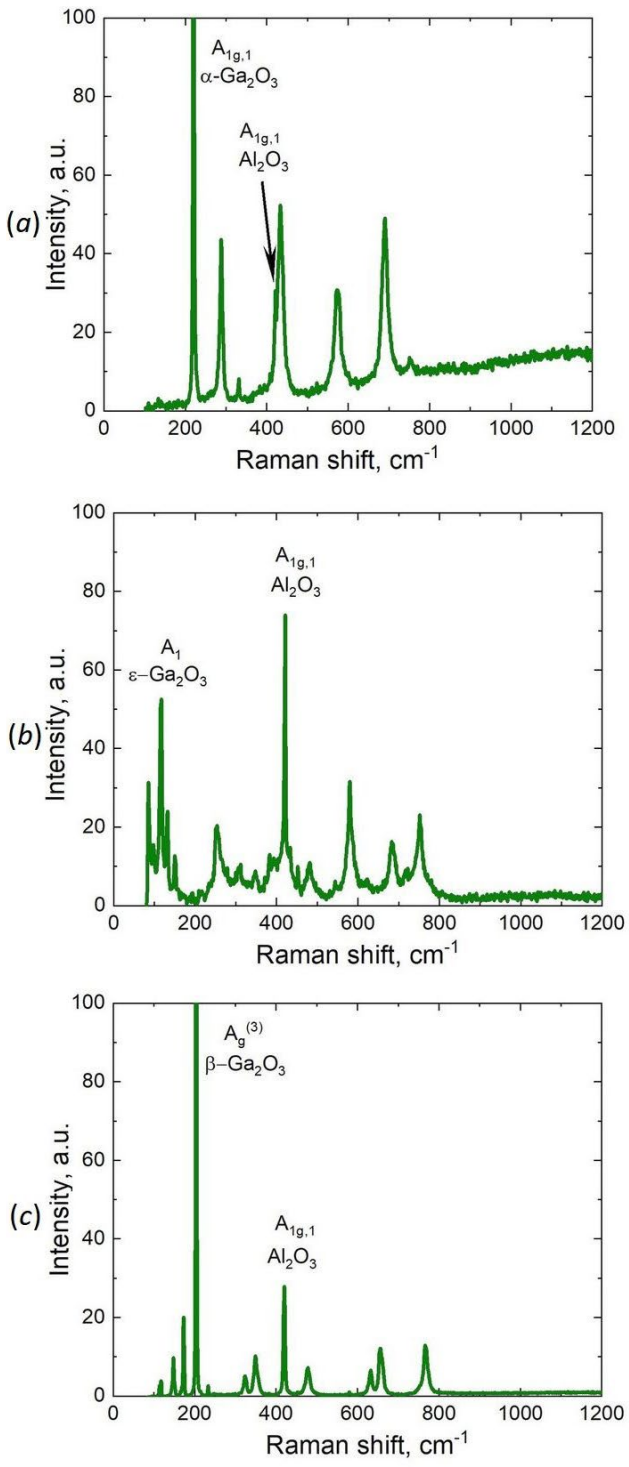

Fig. 3. Raman spectra of three Ga_2O_3 samples grown on Al_2O_3(0001) sapphire at temperatures of 510 (a), 575 (b), 900 °C (c). The main lines of each phase and sapphire are signed

β-phase within 10 min during annealing, starting at a temperature of 650 °C. The X-ray diffraction pattern of the ε-phase sample after annealing for 10 min at 650 °C is shown in Fig. 4. With high temperatures and high annealing times, the result did not change. It is interesting to note that after annealing ε-phase was converted into the β-phase with orientation <$\bar{3}$10> (Fig. 4), whereas during direct growth by the HVPE method, a β-phase was formed with the orientation <$\bar{2}$01> (Fig. 1c). The annealing of the metastable α-phase proceeds completely differently. The α-phase film becomes rough and cracks. Transitions into a stable β-phase did not occur. Complete cracking followed by shedding of the film at a temperature of 750 °C occurred in approximately 25 min, and at a temperature of 850 °C within 10 min. Annealing at a temperature of 650 °C for 30 min also did not lead to the appearance of the β-phase. The X-ray diffraction pattern and Raman spectrum of the sample of α-phases after annealing at a temperature of 750 °C for 15 min, i.e. immediately before cracking and shedding of the film is shown in Fig. 5. It can be seen that of any crystalline phases, only sapphire, i.e., the substrate material is present. High-energy electron diffraction of this sample also revealed only the amorphous phase on the surface. It was impossible to carry out ellipsometric analysis of this sample due to the enormous surface roughness. Thus, we can conclude that instead of the non-crystalline β-phase, the intermediate amorphous Ga_2O_3 phase was formed as a result of annealing of the α-phase and transition of this phase into the β-phase never occurs.

The results obtained can be explained by the difference in phase density. Simulations carried out using the density functional theory [7], allows to determine the density values of each phase with high accuracy. The least dense is the stable β-phase, its density is equal to

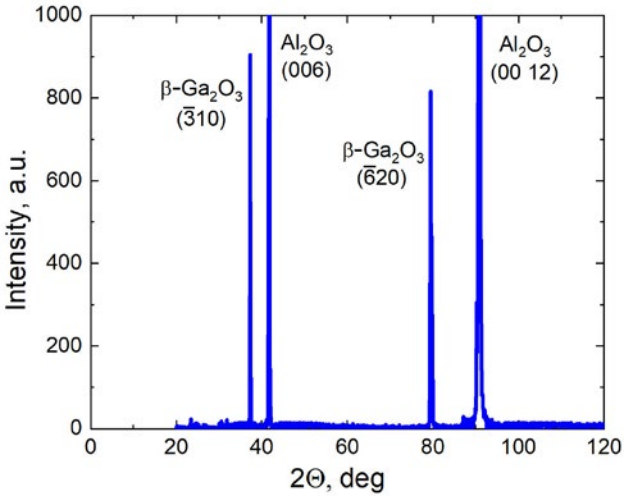

Fig. 4. X-ray diffractogram of ε-Ga_2O_3 sample after annealing for 10 min at 650 °C. It can be seen that the annealing resulted in the formation of β-phase with <$\bar{3}$10> orientation

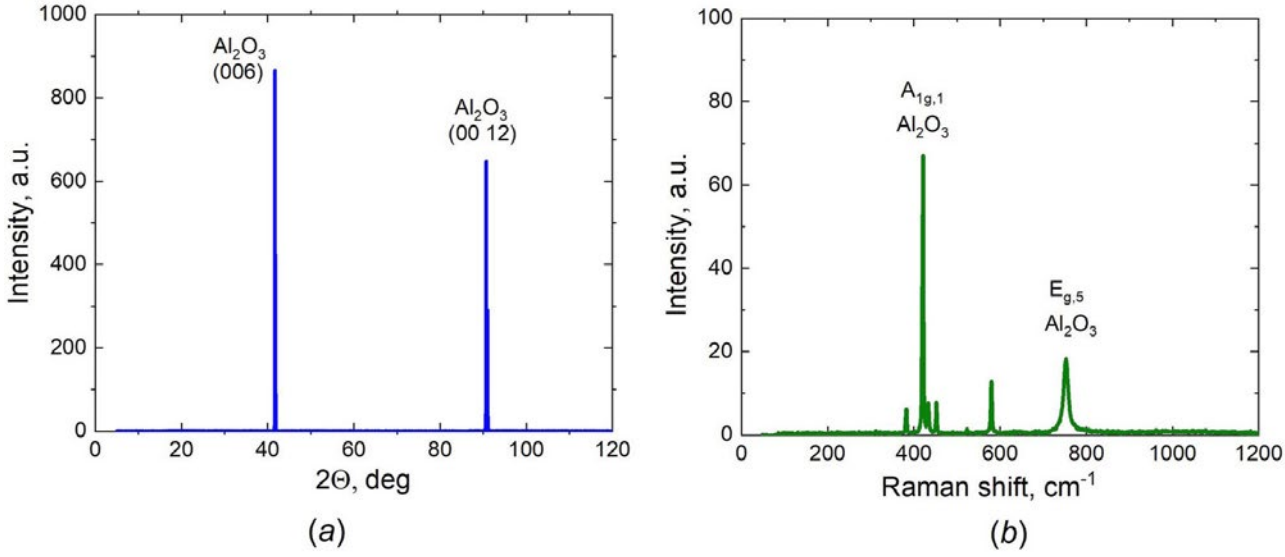

Fig. 5. X-ray diffractogram (a) and Raman spectrum (b) of α-Ga_2O_3 sample after annealing at 750 °C for 15 min. It can be seen that only Al_2O_3 sapphire is present among the crystalline phases

ρ_β = 5.9 g/cm^3, the densest is the most symmetric α-phase, its density is ρ_α = 6.5 g/cm^3, ε the phase is characterized by an intermediate density value ρ_ε = 6.05 g/cm^3. Thus, the reconstructive phase transition from the α into the β-phase was accompanied by a slight increase in volume of about 2.5%. Therefore, it led only to weak, almost imperceptible cracking of the film, which accompanies the phase change. Reconstructive phase transition from the ε into the β-phase was already accompanied by a significant increase in volume of about 10%. Such an increase cannot occur, since the emerging elastic stresses sharply increase the value of the phase transition barrier. As a result, an intermediate amorphous phase is formed, obviously with an intermediate density value, after which the film is destroyed.

4. Conclusions

It is shown that reconstructive phase transitions in Ga_2O_3 into a stable and least dense β-phases proceed in completely different ways. Transition from ε-phases into the β-phase with a decrease in density by 2.5% occurred quite easily and quickly already at a temperature of 650 °C. Transition from α-phases into the β-phase with a decrease in density by 10% proceeded more difficultly. Under the action of huge elastic stresses, the transition only into an intermediate amorphous phase occurred, after which the sample was destroyed without passing into a stable β-phase. Thus, in this study, we concluded that elastic stresses play a decisive role in reconstructive phase transitions by increasing the height of the nucleation barrier. With the significant increase in volume, the transformation may not occur at all.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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